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Microporous and Mesoporous Materials

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Hierarchical ZnO Structures Templated with Amino Acid Based Surfactants

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ABSTRACT

Three different amino acid surfactants were prepared from a coupling reaction of lauroyl chloride with aspartic acid, glutamic acid, and alanine. The newly synthesized amino acid surfactants were used to template zinc oxide nanostructures using a simple sol-gel reaction. The use of amino acid surfactants with different side chain functionalities produced various ZnO structures. The differences in the molecular geometry of the surfactants, along with hydrophilic head group charges are responsible for the formation of spherical and filamentous mesoporous structures of ZnO. The morphologies of ZnO structures were further explored by using different solvents to change packing parameters and micellization behaviors of surfactants. The use of amino acid based surfactants with various head group functionalities opens the potential use of amino acid-based surfactants for templating various metal oxide nanostructures.

KEYWORDS

zinc oxide, *N*-acyl amino acid, sol-gel, mesoporous structure, surfactant

Simple, efficient, and versatile routes to zinc oxide (ZnO) nanomaterials with controllable crystalline morphologies, orientation, and architectures have been extensively explored using various physical or chemical methods including vapor-liquid-solid growth, thermal evaporation, thermal decomposition, electrochemical deposition, and solution-phase processes.¹⁻⁵ As an important wide band gap semiconductor with a large exciton binding energy, ZnO has many useful properties with a great potential in applications of solar cells, chemical sensors, piezoelectric and optoelectronic devices, and catalysts.⁶⁻⁹ A variety of ZnO nanostructure morphologies, such as nanowires, nanorods, nanotubes, nanobelts, and nanohelices/nanorings have been synthesized.^{10,11} However, many of the previously reported synthesis methods are often limited to the formation of the preferred one-dimension (1D) ZnO nanostructure, due to its highly anisotropic growth rate along the c axis.¹² A new strategy for controlled organization of primary building units into complex nanostructures is urgently needed to meet the expanding demands for ZnO applications.

One promising route to rationally control the mesoscale structure of metal oxides is through the use of structure-directing amphiphiles such as low molecular weight surfactants or block copolymers.¹³⁻¹⁶ Introduction of mesoporosity templated with surfactants can drastically enhance the surface area available for interfacial processes compared to solid nanostructures. There are many successful examples of silica and non-silica mesoporous nanomaterials (e.g., oxides of Mn, Al, Ti, Nb, Ta, Zr, Hf, and Sn).¹³⁻¹⁶ However, there are difficulties in the preparation of mesoporous ZnO using surfactants as templates resulting from insufficient interactions between surfactants and inorganic precursors. In addition, the condensation kinetics and chemistry of the ZnO precursors often leads to undesirable macro-scale phase separation that disrupts the co-assembly process.^{15,16} Previously, Choi et al. observed that the use of anionic surfactants (sodium salts of dodecylsulfate, dodecylbenzenesulfonate, 1-hexadecanesulfonate, dioctyl sulfonsuccinate, and monododecyl phosphate) led to the construction of lamellar structured ZnO films while cationic surfactants or nonionic surfactants failed to incorporate any ordered mesostructures into ZnO deposits. Despite extensive survey of experimental conditions (i.e., surfactants, concentrations, organic cosolvents, salts, and pH) to cause a dramatic modification in the stability, curvature, and packing of micellar structures in solution, only lamellar structured ZnO plates

with a lateral dimension of 1-4 μm were formed.^{17,18} In this regard, long chain *N*-acylamino acids are a promising class of surfactants for templating ZnO nanostructures. It is expected that the combination of a different amino acid with various hydrophobic tail chain lengths will allow a simple and versatile route to tune molecular geometry and intermolecular (hydrophilic/hydrophobic, Coulombic, H-bonding) and interfacial interactions between surfactants and inorganic precursors. This new class of surfactants with an amino acid head group and a hydrophobic tail groups are inspired by biomimetic approaches which have successfully shown to form complex organic/inorganic superstructures using amino acids and peptides.¹⁹⁻²¹ Herein, we explore a sol-gel route synthesis of mesoscale ZnO structures using several anionic *N*-acyl amino acids with a different molecular geometry to expand the scope of possible morphologies that can be obtained during supramolecular assemblies.

Results and Discussion

Figure 1a shows the synthesis of long chain *N*-acyl amino acids, **3**, from the reaction of lauroyl chloride, **1**, with different amino acids, **2**, in a mixed solvent of water and acetone, similar to literature procedures.^{22,23} In this study, two anionic amino acids with carboxylic group in the side chain, **R**, aspartic acid, **2a**, and glutamic acid, **2b**, as well as one non-polar amino acid, alanine, **2c**, were selected to cause a gradual variation in the molecular geometry of amino acid surfactants, **3a-3c**. One of the decisive factors in determining mesophases is the molecular packing parameter of ionic surfactants, g

($= \frac{V_0}{a_e l_0}$), where V_0 and l_0 are the volume and the length of surfactant tail and a_e is the effective surface area of the hydrophilic head group of the aggregate expressed per molecule in the aggregate.²⁴⁻²⁶ It is widely used to account for the formation of different mesophases: $0 \leq g \leq 1/3$ for sphere, $1/3 \leq g \leq 1/2$ for cylinder, $1/2 \leq g \leq 1$ for bilayer, and $g \geq 1$ for reversed micelles.²⁴ For common surfactants, the ratio

$\frac{V_0}{l_0}$ is a constant independent of tail length, equal to 21 \AA^2 for single tail and 42 \AA^2 for double tail.²⁵

Therefore the effective headgroup area a_e , which is governed by steric, ionic charge and solvent interaction of the hydrophilic moiety, largely influences the overall molecular packing parameter.

However, the role of surfactant tail group should not be ignored since it also plays a significant role in governing the equilibrium aggregate structure through an explicit or implicit control on a_e or g .²⁶ The newly synthesized amino acid surfactants, *N*-lauroyl-aspartic acid, **C₁₂-asp**, and *N*-lauroyl-glutamic acid, **C₁₂-glu**, have two hydrophilic COOH groups, while *N*-lauroyl-alanine, **C₁₂-ala**, is consisted of one COOH and a CH₃ moieties. For comparison purposes, sodium dodecyl sulfate, **SDS**, and dioctylsulfosuccinate, **SDOS**, were also used as controls. **SDS** has a linear molecular geometry composed of anionic hydrophilic head group and a single hydrophobic tail group, while **SDOS** has same anionic head group with bulkier hydrophobic tail group compared to **SDS**, providing two distinctly different molecular geometry with similar head groups.

Figure 1b through 1g show the SEM images of ZnO precipitates obtained from methanol solutions of Zn(NO₃)₂·6H₂O and surfactants with varying degrees of hydrophobic/hydrophilic ratios. While a typical synthesis of ZnO using Zn(NO₃)₂·6H₂O without any surfactant formed a ZnO gel comprised of platelets (Figure 1b),²⁷ the distinctive change in the macroscopic morphologies resulted with the use of **C₁₂-asp** and **C₁₂-glu** surfactants. Hollow spherical ZnO structures with meso/macro porosity were formed when methanol solution of **C₁₂-asp** was used during synthesis (Figure 1c). The use of **C₁₂-glu** in the same condition resulted in the formation of filamentous precipitates with diameters in the 100 nm range (Figure 1d). However, the **SDS** with a single anionic head group formed only “sheet-like” precipitates, similar to a previous report (Figure 1e).^{17,18} In the structures prepared from **C₁₂-ala** or **SDOS** with a dominant hydrophobic moiety, thin flakes sometimes came together to give a “flower-like” clusters (Figure 1f and 1g).¹⁷ This result indicates that the molecular geometry of surfactants as well as head group charges are important factors which affects the cooperative assembly between the surfactants and ZnO.

Figure 2a shows small-angle X-ray scattering (SAXS) patterns of ZnO assemblies templated with various amino acid surfactants. In all cases, a scattering peak at low 2θ was clearly observed, indicating that the head groups of surfactants cooperatively interact with the oppositely charged zinc species by

using charged ions/species as a mediator under the reaction condition to effectively form ZnO structures with ordered mesophases.^{17,28} From the presence of high-order $00l$ peaks with d_{00l}/l , all the scattering patterns are indexed as lamellar phases with spacings of $d_{001} = 2.83, 2.96, 3.40, 3.91, 3.62$ nm for ZnO templated with **C₁₂-asp**, **C₁₂-glu**, **C₁₂-ala**, **SDS**, and **SDOS**, respectively. The ZnO deposited with **C₁₂-glu**, **C₁₂-ala**, and **SDS** showed the second lamellar phases with d_{001}^* , indicating two distinctively stable bilayer arrangements exist under the given deposition condition.^{17,18} The presence of the second peak depended on compositions of solution, and the high-order peaks for both phases were also observed, similar to previous report.¹⁸ High-resolution TEM image for a selected sample prepared from **C₁₂-asp** confirmed the formation of well-defined lamellar structure (Figure 2b). Wide-angle X-ray diffraction (WAXD) pattern of ZnO samples prepared with surfactants did not show the expected crystalline ZnO. WAXD data of ZnO samples prepared with anionic amino acid surfactants showed broad peaks indicating the amorphous nature of ZnO (Figure S1 in the Supporting Information). This suggests that the carboxylic head groups of **C₁₂-asp** and **C₁₂-glu** surfactants strongly interact with the inorganic species under our condition to effectively stabilize the phase transition to more stable crystalline ZnO, while maintaining the mesoscale structure. The samples prepared with weaker interaction between the head groups and ZnO precursors, **C₁₂-ala**, **SDS**, **SDOS** resulted in the formation of crystalline zinc nitrate hydroxide (PDF 025-1028), which is a precursor phase of ZnO. Thermally driving the precursor phase to form crystalline wurzite structure of ZnO resulted in the collapse of the lamellar structure.

An added benefit to the use of supramolecular assembly assisted synthesis of inorganic materials based on structure-directing amphiphilic molecules is the simplicity to tune and optimize the nanostructures of inorganic materials by changing the experimental variables such as solvents and/or reaction conditions.¹⁴ Figures 3a shows that filamentous ZnO nanostructures were formed when water was used as a solvent for **C₁₂-asp**, instead of the spherical structure from methanol solution of the same surfactant. The structure/morphology differences by changing the solvents can be attributed to the solubility of the **C₁₂-asp** in methanol and water as well as the dependency of the specific area, a_e , on solution conditions. From equilibrium considerations of minimum free energy and Debye-Huckel form

of the electrostatic interaction energy between head groups, Nagarajan reported that the equilibrium area, a_e , per molecule was written as eq (1):²⁶

$$a_e = \left(\frac{\alpha}{\sigma} \right)^{1/2} = \left[\frac{2\pi e^2 d}{\varepsilon \sigma} \frac{1}{1 + kl_0} \right]^{1/2} \quad (1)$$

where α is the headgroup repulsion parameter, σ is a contact free energy per unit area, e is the electronic charge, d is the capacitor thickness in the double layer model, ε is the dielectric constant of the solvent medium, k is the inverse Debye length, and l_0 is the tail length. **C₁₂-asp** has a higher solubility in methanol (with a dielectric constant, ε , of 32.7), which increases the area a_e and decreases the packing parameter, g , thus providing spherical assemblies compared to the filamentous ZnO structure observed in water (ε of 80.1). With this understanding, morphology of **C₁₂-glu** mediated synthesis of ZnO was further explored by changing the solvent from methanol to ethanol (ε of 24.5). Spherical ZnO nanostructures were obtained when ethanol solution of **C₁₂-glu** was used to synthesize ZnO due to higher solubility of **C₁₂-glu** and a larger a_e value in ethanol compared to methanol (Figure 3b). This solvent study shows that the determination and the use of ideal solvent are important steps to obtain desirable structures, as changes in solvent system can induce a preferential enlargement of either hydrophilic head groups or hydrophobic tail groups and change the packing parameters of surfactant molecules during micelle formation, which eventually transform the macroscopic morphologies of ZnO assemblies.

SEM images on several broken pieces for samples obtained from methanol solution of **C₁₂-asp** show porous internal structures of ZnO spheres containing secondary internal pores (Figure 4a and 4b and Figure S2). Individual ZnO filamentous precipitates obtained from the methanol solution of **C₁₂-glu** could be further clustered to give a “network” with a number of interstitial pores by redispersing the as-prepared sample in methanol followed by sonication and subsequent deposition on wafer (Figure 4c and 4d and Figure S3). The main finding of this study is that the use of amino acid surfactants to modify a molecular geometry of surfactant causes the change in macroscopic morphologies of surfactant/ZnO assemblies from typical sheet-like to filamentous to hollow spheres with ordered lamellar mesophases.

The use of anionic amino acid based surfactants alone did not provide a complete control over the organization of periodic ZnO materials such as hexagonal and cubic mesophases. These morphological transformations are associated with changes in the curvature of interfaces and may be understood phenomenologically as a competition between (i) favorable driving force to form organic/inorganic co-assemblies (i.e., interactions between surfactants and inorganic precursors and their stability) and (ii) repulsive force resulting from structural constraints of interfacial and charge separation (i.e., crystallization or macro-scale phase separation). Possible formation mechanism and pathway to amino acid surfactant/ZnO assemblies are i) initial formation of ZnO nanoclusters, ii) interaction of ZnO nanoclusters with micelles, iii) subsequent packing-directed growth of ZnO to a basic unit such as ZnO hollow spheres or cylinders, and iv) final hierarchical organization/aggregation into larger ZnO particles (Figure 4e). The formation and growth mechanism on lamellar mesophases can be attributed to the preferential growth of ZnO along the selected direction and the effect of selective interaction between the inorganic precursors and anionic functional groups of surfactants during the growth of ZnO. It is clear that the dramatic changes in the macroscopic morphologies in ZnO precipitates were caused by the variation in the packing parameters of the amino acid based surfactants and by changing the synthesis conditions, affecting the shapes of the dominant surfactant structures.

CONCLUSIONS

In summary, we explored the use of long chain *N*-acyl amino acids as a new class of surfactant for templating ZnO nanostructures. Formation of different morphology of ZnO was observed from the gradual variation in the molecular geometry and hydrophobic/hydrophilic properties of the surfactants used during the synthesis. This approach expands the possible morphologies of ZnO from typical sheet-like precipitates to filamentous networks to mesoporous spherical superstructures with secondary pores in tens of nm size. The macroscopic structures of ZnO precipitates were also influenced by experimental variables such as solubility and solvents, which control the micellization behavior of surfactants. This study demonstrates a new promising sol-gel route to rationally control mesoscale structures with mesoporosity, which can eventually enhance the surface area of zinc oxide, leading to potential

applications such as solar cells, chemical sensors, piezoelectric and optoelectronic devices, and catalysts.

METHODS

Long chain *N*-acyl amino acids were prepared from the reaction of lauroyl chloride with acidic amino acids in a mixed solvent of water and acetone, as similarly to the literature procedure.^{22,23} Typically, amino acid and sodium hydroxide were first dissolved in water under ice, and then lauroyl chloride dissolved in acetone was added dropwise and stirred overnight. The final composition of acetone in mixed solvent were controlled to be about 0.3~0.4 (vol%). At the end of reaction, HCl was added to the reaction mixture to bring pH 1. The precipitated crude product was filtered off, washed with petroleum ether, and recrystallized. The resulting surfactants were soluble in DMSO and characterized by ¹H NMR spectroscopy. Full details on the preparation and characterization of amino acid surfactants are described in the Supporting Information.

Mesoporous ZnO precipitates were prepared by directly dissolving surfactants and Zn(NO₃)₂·6H₂O in a selective solvent at 60°C followed by the addition of propylene oxide (PPO) acting as a gelation agent.^{27,29} Typically, surfactant (0.5 g) and Zn(NO₃)₂·6H₂O (0.6 g, 1 eq) were dissolved in the solvent (e.g., 2.26 g of methanol) and stirred for 1 hr at 60°C, and PPO (1.16 g, 10 eq to Zn(NO₃)₂·6H₂O) was added. The solution was allowed to gel undisturbed for 1-2 days at 60°C. Then, the aged gels were washed with excess of methanol, filtered, and dried in the oven. For the TEM and SEM observations, ZnO powers were observed in the as-prepared powder on a carbon tape or re-dispersed in methanol, dropped on a carbon-coated grid or a gold-coated Si wafer, respectively, and then dried in the oven. X-ray diffraction analysis (XRD) was performed on powder samples with Rigaku Geigerflex X-ray diffractometer fitted with a Cu K α source.

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SUPPORTING INFORMATION AVAILABLE: Details on the experimental procedure for the synthesis of *N*-acyl amino acid surfactants, and additional results on SEM images and wide-angle X-ray diffraction patterns of ZnO materials. This material is available free of charge via the Internet at <http://pubs.acs.org>

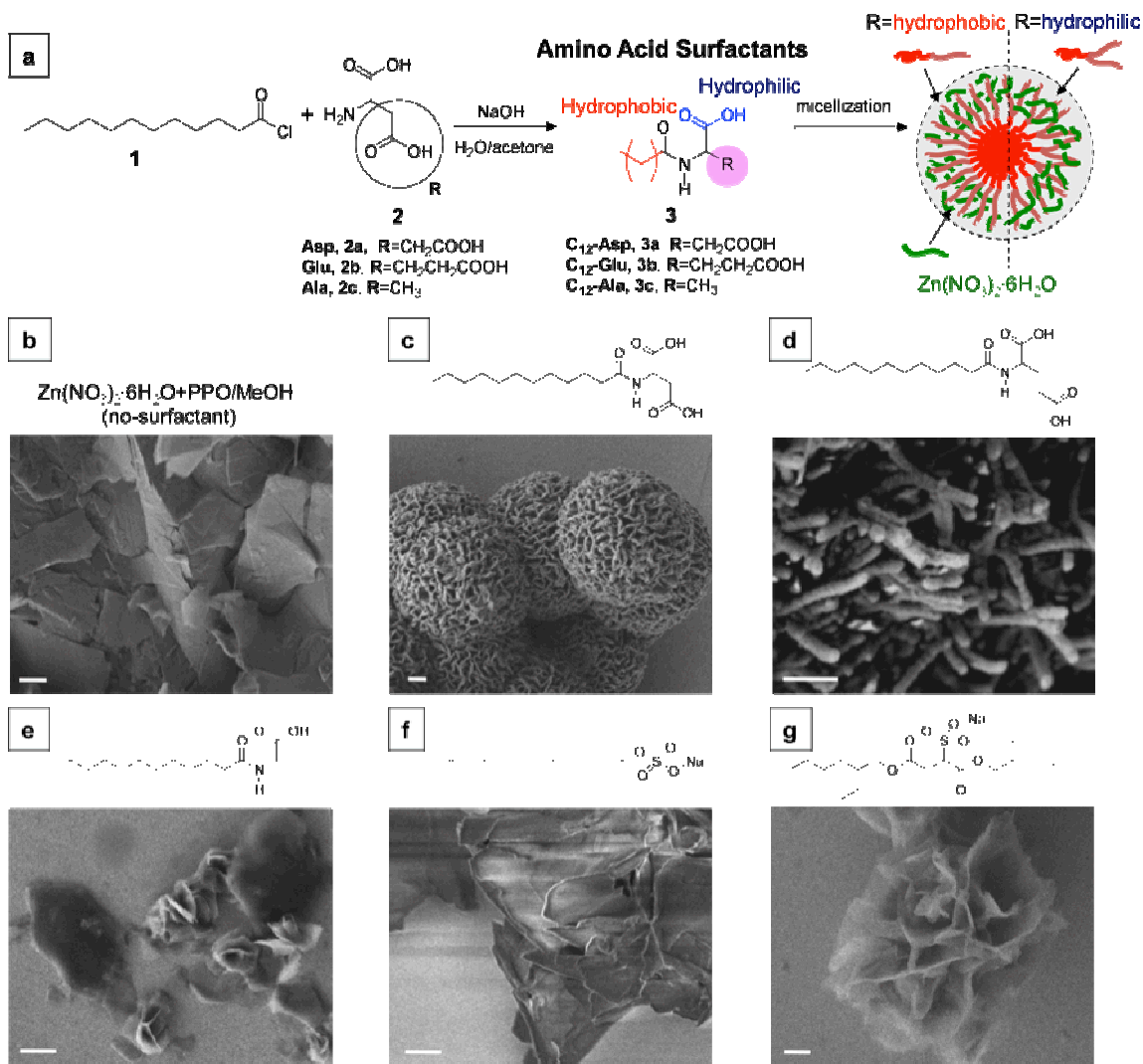


Figure 1. Amino acid tagged anionic surfactants as templates for mesoporous ZnO assemblies. (a) Long chain *N*-acylamino acids were prepared from the reaction of fatty acid chloride and amino acid with different hydrophilic side groups. (b-g) ZnO precipitates prepared from methanol solutions of Zn(NO₃)₂·6H₂O and surfactants: b) samples with no surfactant, c) *N*-acylamino acids tagged with aspartic acid (C₁₂-asp), d) glutamic acid (C₁₂-glu), e) alanine (C₁₂-ala) and commercial anionic surfactants of f) sodium dodecyl sulfate (SDS), and g) sodium dioctylsulfosuccinate (SDOS). Scale bars are 1 μm (b-g).

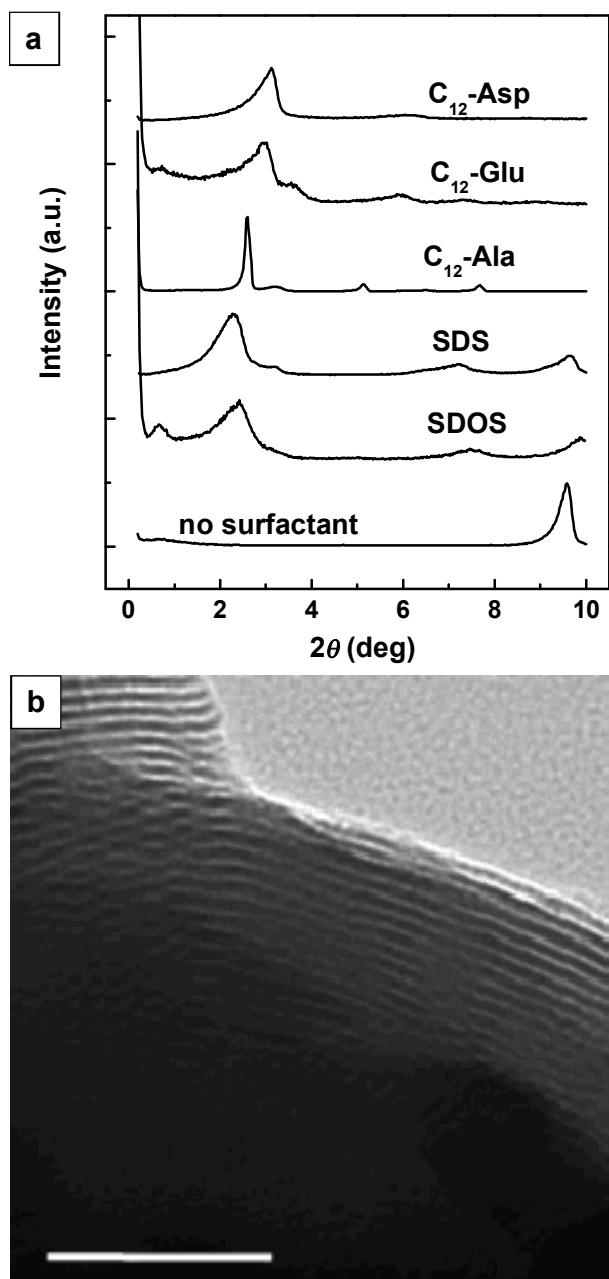


Figure 2. Formation of ZnO mesophases. (a) XRD patterns of ZnO assemblies prepared from mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and surfactants and (b) High-resolution TEM image for selected ZnO sample prepared from C_{12} -asp. The scale bars are 50 nm.

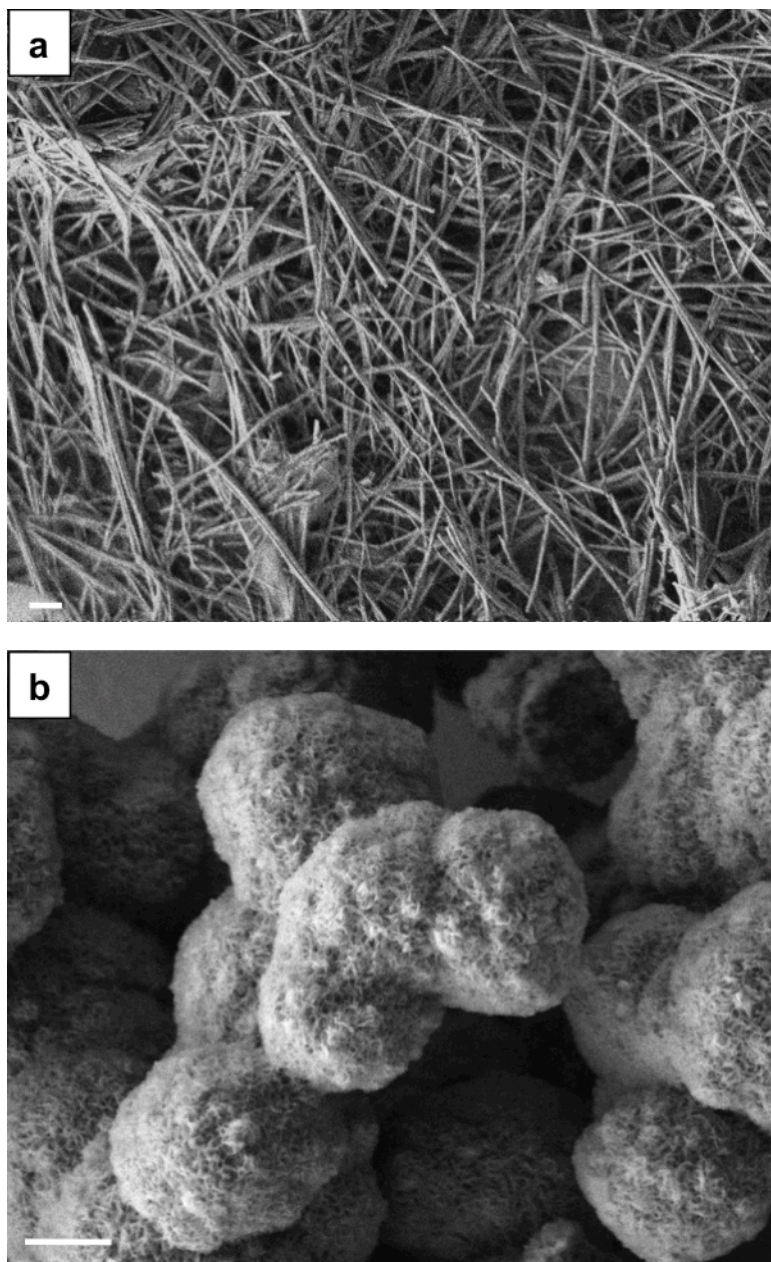


Figure 3. Effect of the selectivity of solvent on morphologies of ZnO structures: (a) **C₁₂-asp** in water and (b) **C₁₂-glu** in ethanol. Scale bars are 1 μm (a,b).

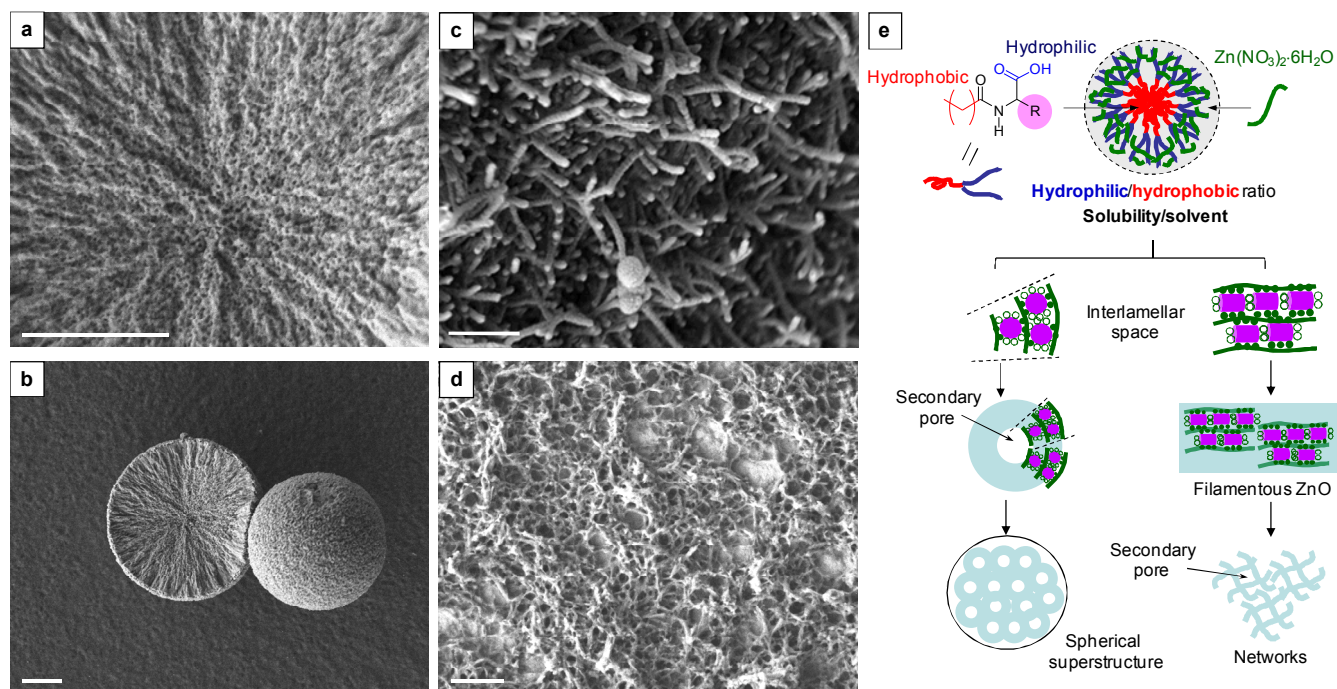


Figure 4. Hierarchical supermolecular ZnO structures prepared from C_{12} -asp (a,b) and C_{12} -glu (c,d) surfacatants in methanol. (a,b) Selected SEM images on the broken pieces for C_{12} -asp/ZnO sample show porous internal structures of ZnO spheres. (c) Filamentous ZnO structures are observed in C_{12} -glu/ZnO sample and (d) redispersing the as-prepared sample in methanol followed by sonication and subsequent deposition of the solution on Si wafer causes individual cylinders to cluster and give a network structure with interstitial pores. (e) Schematic illustration of the proposed formation mechanism for spherical or filamentous ZnO structures through spherical or cylindrical micellar assemblies followed by initial growth of ZnO lamellae and further organization into large particles. Scale bars are 1 μm (a-d).

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SYNOPSIS TOC

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